

Effect of cylindrical geometry on the wet thermal oxidation of AlAs

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We have investigated the wet thermal oxidation of AlAs in cylindrical geometry, a typical configuration for vertical-cavity surface-emitting lasers. Through both experiment and theoretical calculations, we demonstrate a significantly different time dependence for circular mesas from what has been reported in the literature both in studies of stripes and in a study of circular mesas. We attribute this different time dependence to the effect of geometry on the oxidation. © 1998 American Institute of Physics. [S0021-8979(98)06824-8]

I. INTRODUCTION

Since Holonyak's group demonstrated a stable oxide of AlAs, formed by wet thermal oxidation,¹ there has been much interest in using this technique to create a native oxide for the III-V material system. Although recent research has cast doubts on the feasibility of using this oxide for a metal-oxide-semiconductor (MOS)-type device,² it has found wide usage in the creation of vertical-cavity surface-emitting lasers (VCSELs). The oxide provides both current confinement and index guiding, producing the lowest threshold³ and highest efficiency⁴ VCSELs ever reported.

Although VCSELs frequently employ circular mesas, most of the oxidation rate studies to date have been conducted with stripes.⁵⁻⁹ In this article, we describe a model for the oxidation of circular mesas. Our model differs from one previously reported,¹⁰ and we believe it more accurately includes the effect of cylindrical geometry upon the oxidation process.

II. BACKGROUND

The model widely accepted for the wet thermal oxidation of stripes containing buried AlAs layers is based on Grove and Deal's model for the oxidation of silicon.¹¹ This model assumes a steady state process so that the flux of oxidant molecules is constant in three components of the oxidation: (1) transport of oxidant molecules to the edge of the mesa; (2) diffusion of oxidant molecules through the already formed oxide; and (3) reaction at the oxide-semiconductor interface. According to this model, the oxidation time can be described as

$$t = \frac{x_o^2}{B} + \frac{x_o}{B/A}, \quad (1)$$

where we have assumed no initial oxide so that x_o , the length of oxide formed, is also the position of the oxide-semiconductor interface. In Eq. (1), B is proportional to the diffusion constant for the reactant traveling through the oxide and B/A is a function of both the supply of water vapor at the edge of the mesa and the reaction rate constant for

oxidation at the oxide-semiconductor interface. From this model, a linear oxidation is thought to represent a reaction-rate-limited process, while an oxidation length which is proportional to the square root of time is believed to indicate a diffusion-limited process.⁷

III. THEORY

In the case of circular mesas, the surface area of the interface changes as the oxidation proceeds, effectively changing the geometry of the oxidation. Therefore, we do not believe that the steady state assumption is valid for the oxidation of circles. As noted by Ochiai *et al.*,⁷ the functional form for the oxidation of stripes, Eq. (1), is composed of a diffusion and a reaction component. The model described in this article treats the movement of the oxidation front in terms of these processes: diffusion of the reactant to the oxide-semiconductor interface and reaction at the interface. We assume that there is an adequate supply of the reactant at the edge of the mesa and that the removal of As-containing products is not the rate-limiting process. We take the oxidation time to be the sum of the time required for reactant atoms to diffuse to the oxide-semiconductor interface and the time required for the atoms to react at that interface:

$$t_{\text{oxidation}}(x_o) = t_{\text{diffusion}}(x_o) + t_{\text{reaction}}(x_o). \quad (2)$$

Our model, as described by Eq. (2), can be applied to the oxidation of stripes or circles. The functional form we obtain for stripes is the same as that of Grove and Deal's model, Eq. (1). However, when our model is applied to the oxidation of circular mesas, we obtain a functional form which differs significantly from that obtained by applying the steady state formalism to both stripes¹¹ and circular mesas.¹⁰ We believe that, because it is not constrained by the steady state assumption, our model accounts more fully for the influence of cylindrical geometry upon the oxidation process.

A. Theoretical reaction time

First, we consider the reaction time by writing an expression for the number of atoms reacted in a time dt_{reaction} :

$$R dt_{\text{reaction}} = \rho dV, \quad (3)$$

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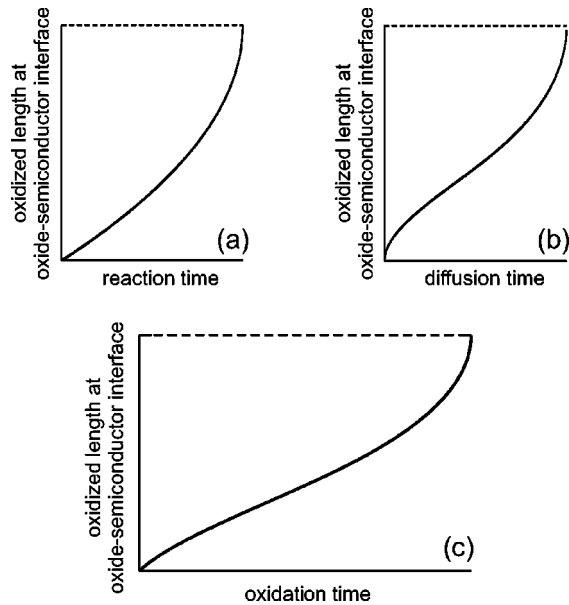


FIG. 1. (a) Functional form for the reaction of oxygen atoms to move the oxide-semiconductor interface in the wet thermal oxidation of AlAs. (b) Functional form for the diffusion of oxygen atoms to the oxide-semiconductor interface in the wet thermal oxidation of AlAs. (c) Functional form for the wet thermal oxidation of AlAs. The dashed line in each plot indicates the oxidized length for complete oxidation (the radius of the mesa).

where R is the reaction rate (in units of atoms per unit time), ρ is the concentration of oxidant molecules in the oxide, and dV is the volume of oxide which must react to move the oxidation front by a differential unit of length. In rectangular coordinates, $dV = L H dx$, where L is the length of the stripe and H is the thickness of the oxidizing layer, while $dV = -2\pi H r dr$ in cylindrical coordinates. Next, we define a rate $K = R/\rho\sigma$, where σ is the outside surface area of the mesa. Therefore, Eq. (3) becomes

$$K dt = dx \quad (4)$$

in rectangular coordinates and

$$K dt = -\frac{r}{a} dx \quad (5)$$

in cylindrical coordinates, where a is the radius of the mesa. Equations (4) and (5) are subject to the boundary condition that no oxide has been formed at $t_{\text{reaction}} = 0$. This condition can be expressed as $x(t_{\text{reaction}} = 0) = 0$ in rectangular coordinates and as $r(t_{\text{reaction}} = 0) = a$ in cylindrical coordinates. Integration and application of the boundary condition in rectangular coordinates yield an expression for the oxidized length, x_o :

$$x_o = K t_{\text{reaction}} \quad (6)$$

In cylindrical coordinates, we obtain

$$x_o = a - \sqrt{a^2 - 2aKt_{\text{reaction}}} \quad (7)$$

where $x_o = a - r$. This curve is shown in Fig. 1(a).

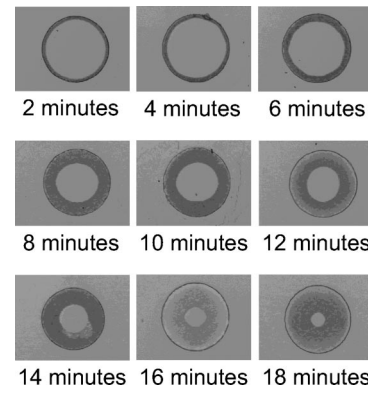


FIG. 2. Optical microscope images of 150 μm diameter mesas, after wet thermal oxidation at 425 $^{\circ}\text{C}$ for the indicated times. The oxidized AlAs layer is viewed through 150 nm GaAs and 15 nm $\text{Al}_{0.3}\text{Ga}_{0.7}\text{As}$.

B. Theoretical diffusion time

Now considering the diffusion time, we assume that the oxidation front (as seen in Fig. 2) occurs where the concentration of oxygen is half that at the edge of the mesa. Choosing some other fraction does not change the functional form of the solution¹² but does affect the absolute value of the diffusion constant obtained for the oxidation. We start with the diffusion equation in rectangular coordinates (assuming only diffusion perpendicular to the oxide-semiconductor interface). Next, the following boundary conditions are applied:

- (1) There is no oxygen inside the mesa when the oxidation begins.
- (2) There is a constant concentration, C_o , of oxygen at the edge of the mesa at all times.

In rectangular coordinates, the solution to the diffusion equation with these boundary conditions is

$$C(x, t) = C_o \left[1 - \text{Erf} \left(\frac{x_o}{2\sqrt{Dt_{\text{diffusion}}}} \right) \right], \quad (8)$$

where D is the diffusion constant for oxygen in the oxide film. In order to obtain $x_o(t_{\text{diffusion}})$, we set Eq. (8) equal to $0.5C_o$, which yields

$$x_o = \sqrt{k_D t_{\text{diffusion}}}, \quad (9)$$

where

$$k_D = 4D[\text{Erf}^{-1}(0.5)]^2. \quad (10)$$

In cylindrical coordinates, the diffusion equation can be written as¹³

$$\frac{\partial C}{\partial t_{\text{diffusion}}} = \frac{1}{r} \frac{\partial}{\partial r} \left(r D \frac{\partial C}{\partial r} \right), \quad (11)$$

where C is the oxygen concentration in the mesa. The boundary conditions can be written as: (1) $C(t=0, r \leq a) = 0$ and (2) $C(r=a) = C_o$. Carslaw and Jaeger give a solution to this problem:¹⁴

$$C(r, t_{\text{diffusion}}) = C_o \left[1 - \frac{2}{a} \sum_{n=1}^{\infty} e^{-D\alpha_n^2 t_{\text{diffusion}}} \frac{J_0(r\alpha_n)}{\alpha_n J_1(a\alpha_n)} \right], \quad (12)$$

where J_n represents the n th-order Bessel function and the $\{\alpha_n\}$ s are solutions to $J_0(a\alpha_n)=0$. We numerically solve the equation $C(r, t_{\text{diffusion}})=0.5C_0$ to obtain an expression for the radius of the oxidation front (and thus the oxidized length) as a function of the diffusion time. The resulting curve is plotted in Fig. 1(b).

C. Oxidation in cylindrical geometry

Following Eq. (2), our oxidation model is completed by summing the diffusion and reaction times for a given oxidation length, x_o . The resulting curve for cylindrical coordinates is plotted in Fig. 1(c). It is clear from this curve that the oxidation of circular mesas is predicted to proceed in a much different manner than that of stripes. While the oxidation rate for steady state models (both circles¹⁰ and stripes¹¹) decreases as the oxidation proceeds, our model predicts that the oxidation rate will increase for cylindrical geometry. In addition, we would like to point out that a similar effect is both expected and observed for square mesas,¹⁵ another typical VCSEL configuration. In both circles and squares, the surface area of the oxidation front decreases as the oxidation proceeds, and this geometric effect causes an increase in the oxidation rate.

IV. EXPERIMENT

A. Sample preparation and data collection

The samples used in this study were grown on a (100) GaAs substrate in a Perkin Elmer molecular beam epitaxy (MBE) machine. The layer to be oxidized was 100 nm of AlAs, surrounded on either side by 15 nm of $\text{Al}_{0.3}\text{Ga}_{0.7}\text{As}$. The structure was capped with 150 nm of GaAs. Circles, 150 μm in diameter, were defined using standard photolithography procedures. Hardened photoresist served as an etch mask when the samples were placed in 1:8:80 $\text{H}_2\text{SO}_4:\text{H}_2\text{O}_2:\text{H}_2\text{O}$ to remove the material around the mesas, exposing the AlAs layer. Each sample was etched immediately prior to being inserted into a 425 $^\circ\text{C}$ furnace which was connected to a 90 $^\circ\text{C}$ water bubbler through which 1 ℓ/min ultrapure nitrogen was flowing. An optical microscope and charge coupled device (CCD) camera were used to obtain images of the mesas. The pictures were then inserted into a drawing program to measure the diameter of the unoxidized portion of each mesa. Sample pictures are shown in Fig. 2.

For each oxidation time, an average of two samples were oxidized in different runs. Each sample contained approximately 30 circles, so each data point represents information from about 60 mesas. There was no systematic difference in oxidation rates for samples oxidized on different days. The data is shown in Fig. 3.

B. Results

We start by noting that the qualitative behavior of our data is quite different from that expected for stripes, particularly for longer oxidation times. The oxidation rate increases as the oxidation front nears the center of the mesa, in agreement with our model, as shown in Fig. 1(c).

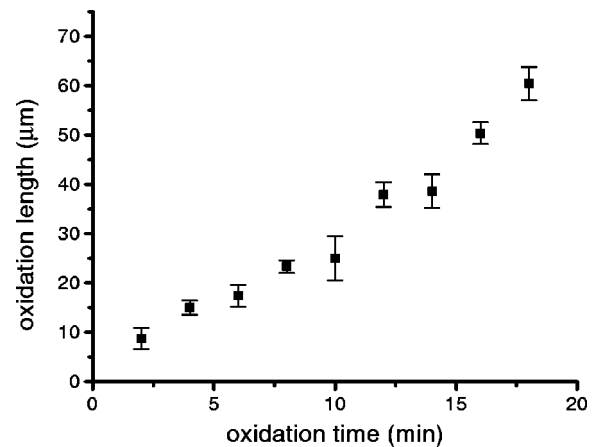


FIG. 3. Measured lateral oxidation length as a function of time for 150 μm diameter mesas oxidized at 425 $^\circ\text{C}$.

In order to compare our data and theory, we fit the data to

$$t_{\text{oxidation}} = t_{\text{diffusion}}(D, x_o) + t_{\text{reaction}}(K, x_o), \quad (13)$$

using D and K as fitting parameters. The resulting curve is shown in Fig. 4, fit using $D = 98 \pm 4 \mu\text{m}^2/\text{min}$ and $K = 5.3 \pm 0.3 \mu\text{m}/\text{min}$.

C. Comparison to oxidation of stripes

Figure 5 shows data for the oxidation of stripes under the same conditions (425 $^\circ\text{C}$ furnace, 90 $^\circ\text{C}$ water bubbler, 1 ℓ/min N_2 flow) as those used to oxidize the circular mesas. Theoretical curves for circles and stripes are also shown. It is clear from Fig. 5 that the oxidation of circles proceeds much faster than that of stripes, particularly for longer times. In order to plot the curve for stripes, we use Eq. (2), with expressions for t_{reaction} from Eq. (6) and for $t_{\text{diffusion}}$ from Eq. (9):

$$t = \frac{x_o}{K} + \frac{x_o^2}{k_D}, \quad (14)$$

with $D = 98 \mu\text{m}^2/\text{min}$. We obtain $K = 3.9 \pm 0.2 \mu\text{m}/\text{min}$, which is in reasonable agreement with the value obtained for

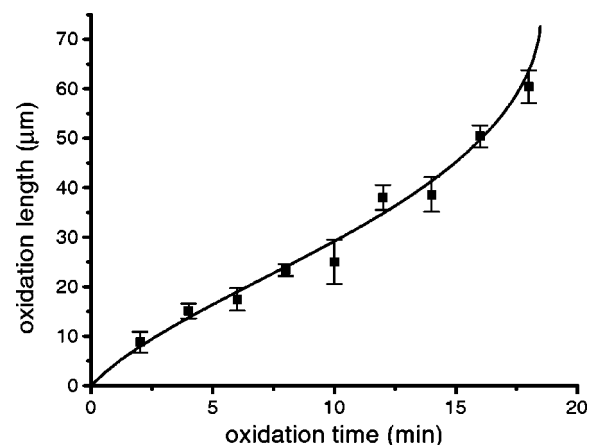


FIG. 4. Model and experimental data for the wet thermal oxidation of AlAs at 425 $^\circ\text{C}$, with $D = 98 \mu\text{m}^2/\text{min}$ and $K = 5.3 \mu\text{m}/\text{min}$.

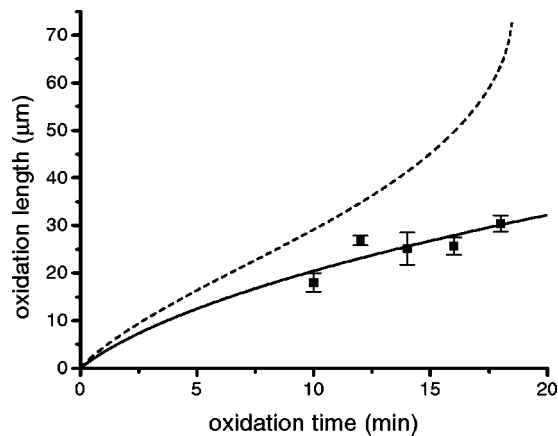


FIG. 5. Measured lateral oxidation length as a function of time for stripes oxidized at 425 °C shown with theoretical curves for both stripes and circular mesas with $D=98 \mu\text{m}^2/\text{min}$. The solid line indicates theory for stripes with $K=3.9 \mu\text{m}/\text{min}$ and the dashed line indicates theory for circular mesas with $K=5.3 \mu\text{m}/\text{min}$.

circles. We would expect both D and K to show agreement between circles and stripes since the oxide's resistance to the diffusion of oxygen and the reactivity of AIs with oxygen should not be influenced by geometry.

We can use this data to compare our experimental results to those obtained by other researchers for studies involving stripes by comparing Eq. (14) with Grove and Deal's model in Eq. (1). In Grove and Deal's model, $k_D=B$. We can use Eq. (10) to calculate k_D for our model with $D=98 \mu\text{m}^2/\text{min}$, which yields $k_D=89 \mu\text{m}^2/\text{min}$. A study by Naone *et al.*¹⁶ found $B=59 \mu\text{m}^2/\text{min}$ for oxidation of AIs at 425 °C with a 90 °C water bubbler and 0.6 ℓ/min N_2 flow. Extracting data from Fig. 4 of Ref. 7 yields B on the order of $100 \mu\text{m}^2/\text{min}$ for oxidation of AIs at 425 °C with an 85 °C water bubbler and 0.8 ℓ/min N_2 flow. Therefore, the k_D we obtained for both stripes and circles is in reasonable agreement with values obtained by other researchers for stripes.

Similarly, we can compare the value of K we obtained for circles and stripes with that obtained by other researchers. In Grove and Deal's model, $K=B/A$. Naone *et al.*¹⁶ report $B/A=1.1 \mu\text{m}/\text{min}$ and data extracted from Ochiai's paper⁷ indicates $B/A=6.7 \mu\text{m}/\text{min}$. Our values of 5.3 and $3.9 \mu\text{m}/\text{min}$ fall between these values.

As shown by other researchers,^{7,11} the oxidation of stripes is reaction rate limited for short times and diffusion limited for longer times. We would expect the same behavior for circular mesas, despite the different time dependence of the oxidation. The reaction and diffusion components of the oxidation of circular mesas are shown in Fig. 6. We can see that, for oxides thinner than $20 \mu\text{m}$, the reaction is the slower process contributing to the oxidation; but, after $20 \mu\text{m}$ of oxide has been formed, diffusion of atoms to the interface takes longer than their reaction once at the interface. Our oxidation of stripes also exhibits a transition between reaction and diffusion processes around the same oxidized length. In addition, as observed in the case of the oxidation of stripes, we see that the oxidation curve has a time dependence similar to that of the reaction process for small times

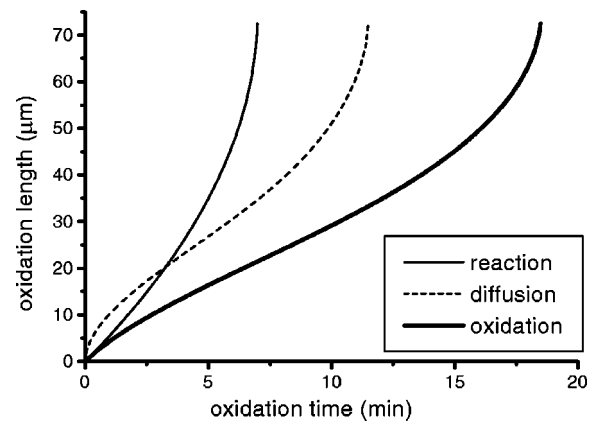


FIG. 6. Reaction curve (light solid line) for $K=5.3 \mu\text{m}/\text{min}$, diffusion curve (dashed line) for $D=98 \mu\text{m}^2/\text{min}$, and the resulting oxidation curve (heavy solid line) for circular mesas.

and a time dependence similar to that of the diffusion process for longer times.

As a final comparison to the oxidation of stripes, we believe that the model for the oxidation of circles should reduce to the model for the oxidation of stripes in the limit $\alpha \gg x_o$. In this limit, our model reduces exactly to the form for the oxidation of stripes.

V. CONCLUSIONS

As demonstrated in this article, the oxidation of circular mesas exhibits a significantly different time dependence than that observed for stripes. Although it is possible to determine the appropriate oxidation time for a given VCSEL structure by trial and error, this method becomes difficult for more complicated structures, such as VCSELs with both oxidized Bragg reflectors and oxidized current apertures. Using oxidation rates obtained for stripes will result in overoxidation, particularly for longer oxidation times. We have also shown that, while the cylindrical geometry has a significant effect on the time dependence of the oxidation process, the basic physics of the oxidation remains unchanged. We hope that the different behavior exhibited by the cylindrical mesas will allow for greater understanding of the wet thermal oxidation process.

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